WET PROCESS TECHNOLOGY IV. EVALUATION OF AN ALTERNATIVE DELIMING AGENT*

Abstract

Ammonium sulfate is commonly used to delime hides by the United States tanning industry, a practice that results in elevated levels of ammonia in beamhouse effluent. Concern that eventual restrictions on the levels of ammonia permitted in tannery effluent will be difficult and expensive to meet has led to investigations to find alternative deliming agents. Magnesium sulfate has been suggested as one alternative. While this substitution effectively lowered the concentration of ammonia in the effluent, the quality of the resulting leather has been questioned. The ability of magnesium to replace ammonia in deliming as reported in the literature was examined at ERRC. While differences were found in the resulting leather, modification of the published process produced an acceptable product. The chemical and physical changes which occurred using magnesium sulfate are compared with data from a standard process developed for converting cattlehides to chrome tanned leather using ammonium sulfate. The proposed modification to the process, the resulting analytical data, and the crust leather evaluations are presented.

Introduction

Ammonium sulfate is the chemical of choice in the tanning industry for deliming hides. Concern about the increasing difficulty of meeting restrictions on ammonia in waste streams has led to the development of an alternative deliming method using magnesium sulfate. Koopman suggested that magnesium sulfate in combination with sulfuric acid could effectively remove calcium from limed hides (1-5). Constantin published data which were not in agreement with this work (6-7). He felt that the leather produced using this deliming method was not acceptable. His work demonstrated that one could not simply apply this method to a cattlehide leather-making process without further modification of either the method or the process.

The magnesium sulfate deliming method proposed by Koopman was examined at the bench scale and the pilot scale level. The objective was to see if the method could be modified to correct the objections raised. Chemical tests were done on hide samples during magnesium sulfate deliming and compared with a standard process developed at ERRC (8). The data collected included the chemical composition of the hide and the effluent as well as the physical properties and evaluation of the quality of the resulting leather.

Experimental

Rawstock

The brined hides were obtained from commercial hide brokers.

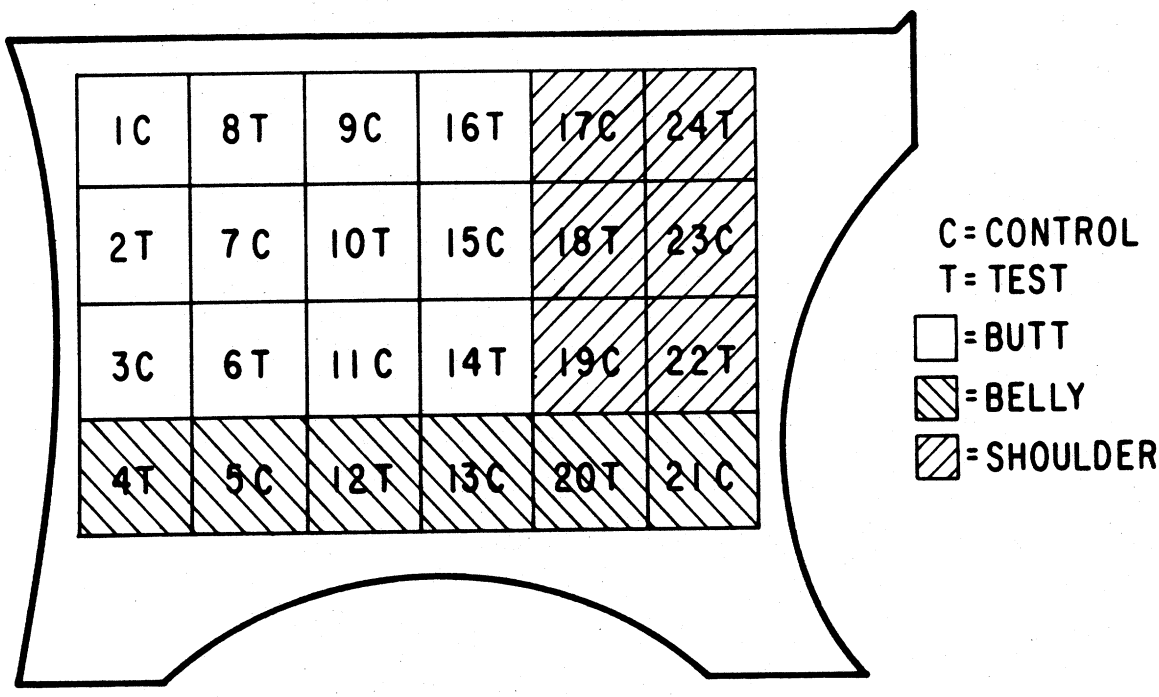

Figure 1. Sectioning of hide and location of samples.

Bench Scale Experiments

Samples approximately 8 by 11 inches were cut from brined hides and labeled as shown in Figure 1. They were processed through the wash after relime along with up to five full sides in a Challenge Cook* stainless steel pilot hide processor using the standard process (8). Test samples were allocated randomly to varying magnesium sulfate and sulfuric acid concentrations. The samples were placed in one gallon plastic jars and the appropriate amounts of magnesium sulfate and sulfuric acid† were added. Magnesium sulfate levels ranged from 1 to 9 percent and sulfuric acid from 0 to 0.6 percent. Samples were tumbled in a temperature controlled Riot drum for 1 1/2 hr. Seven-eighth inch plugs were removed from each sample at 30, 60, and 90 min, and after the wash. The hide pieces were returned to the processor and pickled and tanned with the full sides. Additional samples were taken for analysis after tanning.

*Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

†Caution: Care must be taken when concentrated acid is added to relime samples because of the evolution of H_2S.

Pilot Scale Experiments

These experiments were carried out in the Challenge Cook stainless steel pilot scale hide processor. The standard process was used to bring the hides through the relime stage and through the pickle and tan steps (8). The magnesium sulfate-sulfuric acid deliming step was carried out as follows:

Float		125%
H_2SO_4		0.2%
	Tumble 30 minutes	
	pH 9.0	
$MgSO_4.7H_2O$		3-7%
Oropon W4		0.08%
	Tumble 1 hr	
	pH 9.0	
	Wash IX	
Float		100%

Matched side controls were delimed with ammonium sulfate (8). All sides were brought to the crust by a standard retan-color-fatliquor process (8) or by a process normally used in a cooperating tannery.

Chemical Analyses

Moisture, ash, calcium, chrome and ammonia determinations were carried out as described in a previous publication (9). The analysis of magnesium was carried out on the same samples that were prepared for the calcium determinations. They were analyzed by Atomic Absorption Spectrophotometry as described in the Perkin Elmer manual (10). The high levels of magnesium in the hide required that the 228 mu wavelength be chosen for anaylsis because of its decreased sensitivity. This reduced the necessity for excessive dilutions.

Physical Analyses

Ball Burst, Stitch Tear, and Tensile Strength were carried out on the crust leather as described in a previous paper (11).

Results and Discussion

Bench Scale Experiments

Experiments were carried out to measure the effectiveness of calcium removal by magnesium sulfate and sulfuric acid in the deliming stage. The experiments repeated and

bracketed Koopman's work in terms of concentrations of both magnesium sulfate and the amount of sulfuric acid added. His formula is shown below (1).

Float	50%
Temperature	95°F
H_2SO_4	0.5%
$MgSO_4 \cdot 7H_2O$	7%

Acid added in 10% H_2O in multiple feeds over 30 minutes
Run 15 minutes after last feed
Bate 0.12%
Run continuously for 80 minutes

The results of the calcium determinations consistently showed that at each level of magnesium sulfate and at all levels of sulfuric acid tested approximately 10 percent more calcium was removed by magnesium sulfate than by the ammonium sulfate. Comparisons were always made between each test sample and the control samples immediately surrounding it. The average calcium removals at each level of magnesium sulfate and acid varied with location, the greatest removal being in the less dense areas like the belly and less removal in the denser butt and shoulder areas. The designation of hide parts as shown in Figure 1, is described in the ALCA methods manual (12). Analytical results were com-

TABLE I

EFFECTIVENESS OF MAGNESIUM AND AMMONIUM SULFATE SALTS IN CALCIUM REMOVAL FROM LIMED CATTLEHIDE AT VARIOUS HIDE LOCATIONS

	% Calcium Removed	
Area	$(NH_4)_2SO_4$	$MgSO_4 \cdot 7H_2O$
Butt[a]	41.0	50.4
Belly[b]	42.6	53.4
Shoulder[b]	40.3	51.1

[a] N = 12
[b] N = 6

TABLE II

EFFECTIVENESS OF AMMONIUM SULFATE AND VARYING AMOUNTS OF MAGNESIUM SULFATE IN CALCIUM REMOVAL FROM LIMED CATTLEHIDES

	Percent Calcium Removed		
% $MgSO_4 \cdot 7H_2O$ added	$MgSO_4 \cdot 7H_2O$	$(NH_4)_2SO_4$[a]	Difference
1	61.8	49.8	+ 12.0
3	68.5	51.2	+ 17.3
5	52.6	38.5	+ 14.1
7	44.2	33.0	+ 11.2
9	49.6	39.1	+ 10.5

[a] Controls surrounding magnesium sulfate delimed samples.

bined from these three areas and are shown in Table I. Variations in individual samples over the three time periods were small. Table II contains the percent calcium removed from the hide relative to the amount of magnesium sulfate added. The data suggest that all levels of magnesium sulfate were effective in removing calcium. However, the data could be confounded because of the area in which sampling was carried out, as well as the way sampling was done. To remove several samples from a small hide piece (8" x 11") may cause the calcium to migrate out of the hide in a different manner than when a full side was used. The data suggests that the 3 and 5 percent levels were most effective. The pilot studies support this supposition. Furthermore, the addition of acid did affect greatly the final pH and the addition of 0.6% acid reduced the pH to 3.5. This would be too low since it is necessary for the final solution to be pH 8 or greater to have an active bate.

TABLE III

PERCENT MAGNESIUM FOUND IN HIDE DURING DELIME/BATE

	Percent Magnesium[a]				
% $MgSO_4 \cdot 7H_2O$ added	30 Min	60 Min	90 Min	Wash	N
1	0.12	0.14	0.16	0.13	4
3	0.23	0.32	0.34	0.26	4
5	0.31	0.40	0.49	0.35	8
7	0.44	0.55	0.60	0.46	4
9	0.50	0.77	0.77	0.54	4

[a] Expressed on a moisture free basis (MFB).

It is interesting to observe the uptake of magnesium by the hide pieces during the 90 minute treatment and after the wash as shown in Table III. The data are listed in increasing amounts of magnesium sulfate. There is a definite, as expected, trend toward increasing amounts of magnesium being taken up by the hide as the amount of magnesium added is increased. It was important to determine whether the magnesium would remain in the hide even after bluing. In one experiment samples were taken after chrome tanning for magnesium analysis and in all cases less than 0.01 percent remained. Studies on the full sides will clarify at what stages the magnesium is removed.

The calcium and chromic oxide content of the tanned hide pieces in this experiment were examined. The percent calcium remaining in the hide appears to be consistent no matter what the treatment, the small variations being due to location on the hide. The variations in the chrome content which range from 2.72 to 4.50% for the control and from 2.92 to 4.58% for the test also appear to be related to location.

Several conclusions can be drawn. First, it is obvious that when sampling a hide, one must be consistent in the area from which the samples are taken. In previous work, samples have always been taken from the butt area. This has without doubt contributed to the precise results and the high reproducibility obtained in pilot scale runs on industrial processes (11), as well as the high degree of reproducibility in the standard process (8).

The data show that the magnesium sulfate-sulfuric acid deliming is effective in removing calcium from a relimed hide. They also demonstrate that the amount of magnesium remaining in the blue stock is negligible and should not affect the retan-color-fatliquor. The amount of calcium remaining in the delimed hide from the magnesium treatment is 10 percent less than the control. Chrome uptake appears not to be affected. This is

substantiated by the similarities found in the amount of chromic oxide found in the test and the control pieces.

On the basis of these results the pilot scale tests began with a level of magnesium as recommended by Koopman, and then lower amounts were used. If effective, this would reduce the cost of the treatment and should still achieve the necessary calcium removal.

Pilot Scale Experiments

Several experiments were designed for full sides to test the effectiveness of the magnesium deliming. In each experiment, controls were run on matched sides. Experiments A and B, using 7 and 5% magnesium sulfate respectively, were run simultaneously with the two bench scale experiments. In each experiment the sides and the hide pieces were brought to the bate by the standard process (8), the appropriate deliming was carried out, and the sides and the pieces were pickled and tanned together, again using the standard process.

It was felt that the 0.5% sulfuric acid, as recommended by Koopman would drop the pH too low and the amount that was added therefore was only 0.2%. This resulted in a pH of about 9.0. The analytical data from these two runs are given in Table IV. Both of these formulas were effective in removing the calcium from the relimed hides.

TABLE IV

CHEMICAL ANALYSIS OF STOCK DELIMED WITH MAGNESIUM SULFATE AND WITH AMMONIUM SULFATE

Percent (MFB)	Experiment A		Experiment B	
	Test[a]	Control[b]	Test[c]	Control[b]
Ca in Limed Hides	0.97[d]	0.97	1.28	1.28
Mg in Limed Hides	—	—	0.05	0.05
Ca in Delimed Hides	0.45	0.51	0.61	0.73
Mg in Delimed Stock	0.44	—	0.41	0.03
Ca in Blue Stock	—	—	0.30	0.39
Mg in Blue Stock	—	—	0.01	0.01
Cr_2O_3 in Blue Stock	3.43	2.83	3.39	3.24

[a]Delimed with 7% magnesium sulfate and 0.2% sulfuric acid.
[b]Delimed with 1 1/4% ammonium sulfate.
[c]Delimed with 5% magnesium sulfate and 0.2% sulfuric acid.
[d]The values shown are the average of a minimum of three analyses.

TABLE V

CHEMICAL ANALYSIS OF STOCK DELIMED WITH MAGNESIUM SULFATE AND WITH AMMONIUM SULFATE

Percent (MFB)	Experiment C		Experiment D	
	Test[a]	Control[b]	Test[c]	Control[b]
Ca in Limed Stock	1.04[d]	1.04	1.01	1.01
Mg in Limed Stock	0.05	0.05	0.06	0.06
Ca in Delimed Stock	0.57	0.69	0.56	0.65
Mg in Delimed Stock	0.26	0.02	0.31	0.03
Ca in Blue Stock	0.24	0.24	0.23	0.25
Mg in Blue Stock	0.01	0.01	0.01	0.01
Cr_2O_3 in Blue Stock	3.56	3.62	4.24	3.96

[a]Delimed with 3% magnesium sulfate and 0.2% sulfuric acid.
[b]Delimed with 1 1/4% ammonium sulfate.
[c]Delimed with 4% magnesium sulfate and 0.2% sulfuric acid.
[d]The values shown are the average of a minimum of three analyses.

The results of the bench scale experiments suggested that even lower amounts of the magnesium sulfate could be used. In experiment C, 3% magnesium sulfate was added along with 0.2% sulfuric acid, and Table V shows that this amount was effective in calcium

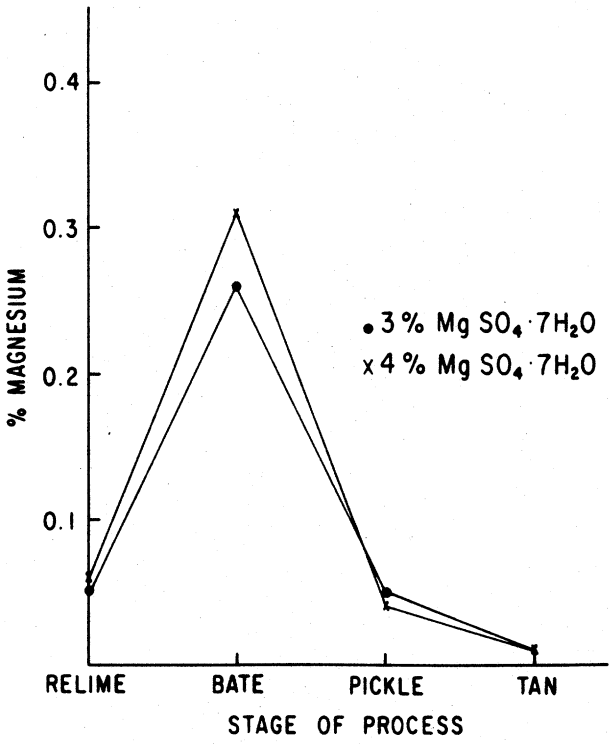

Figure 2. Percent magnesium (MFB) found in hide after each processing stage.

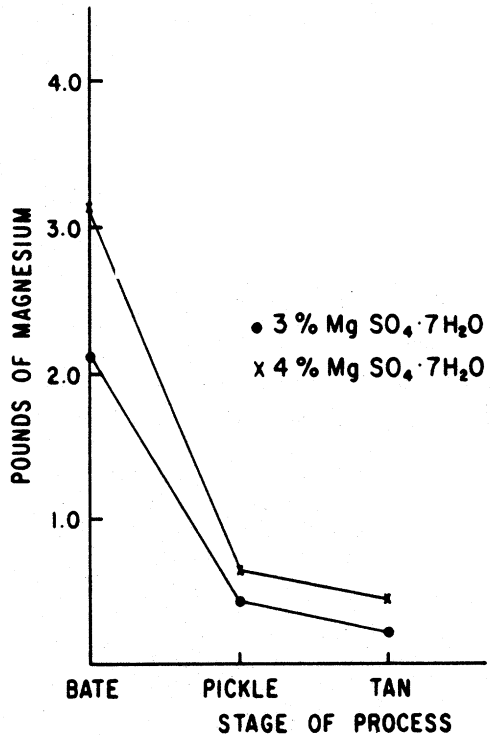

Figure 3. Pounds of magnesium/1000 lbs of hide found in effluent after each processing stage.

removal. However, the crust resulting from this run was not satisfactory and it was decided to increase the magnesium sulfate concentration to 4%. These analytical results are also shown in Table V.

As mentioned before, the stage at which the magnesium was removed needed to be clarified. Samples were taken from these full sides after the relime, bate, pickle, and tan, as well as from the resulting effluent. Graphically, in Figures 2 and 3, the removal of the magnesium from the hide and its appearance in the effluent are shown. The 4% addition shows correspondingly higher amounts in both the hide and the effluent. In Figures 4 and 5, the calcium removal in the hide and its appearance in the effluent by the standard method are compared to the two magnesium delimings. Both figures show graphically the more efficient removal of calcium by magnesium sulfate.

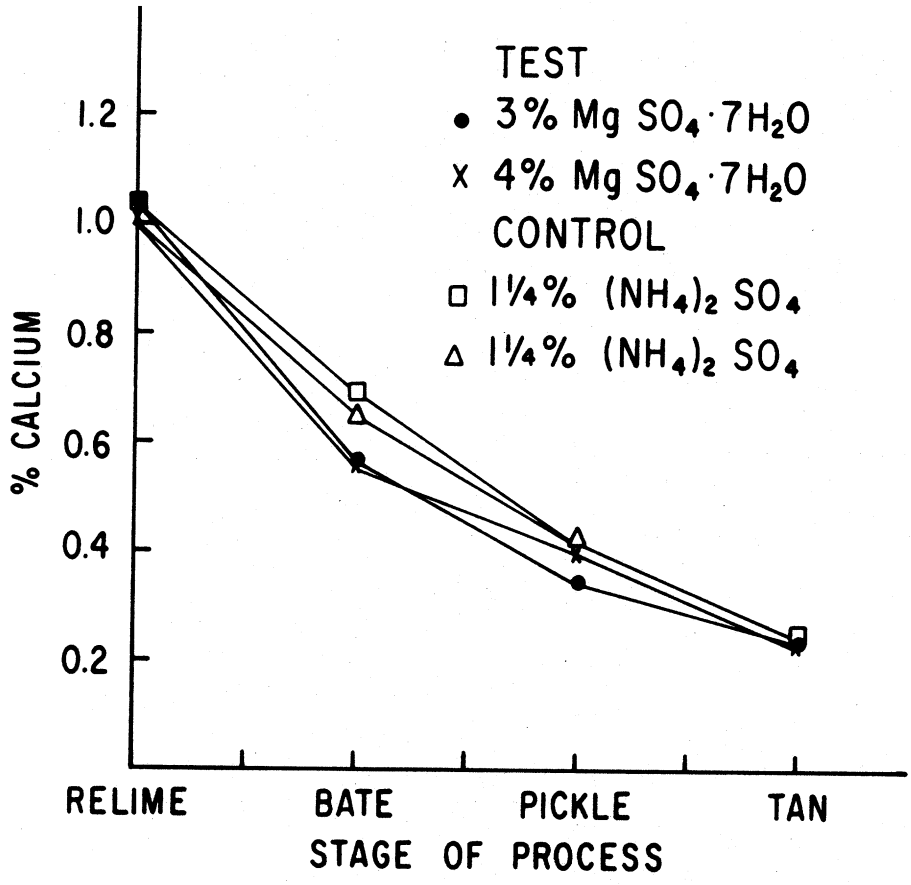

Figure 4. Percent calcium (MFB) found in hide after each processing stage.

Material balances for calcium, magnesium, and chrome were calculated from the data resulting from experiments C and D. The calcium and magnesium balances were calculated from the amount of calcium and magnesium found in the relimed hide, from the calcium and magnesium found in the effluent after the bate, pickle and tan, from the calcium and magnesium added in the recycle chrome and from the calcium and magnesium found in the tanned hide. The chrome balance was calculated from the amount of chrome added

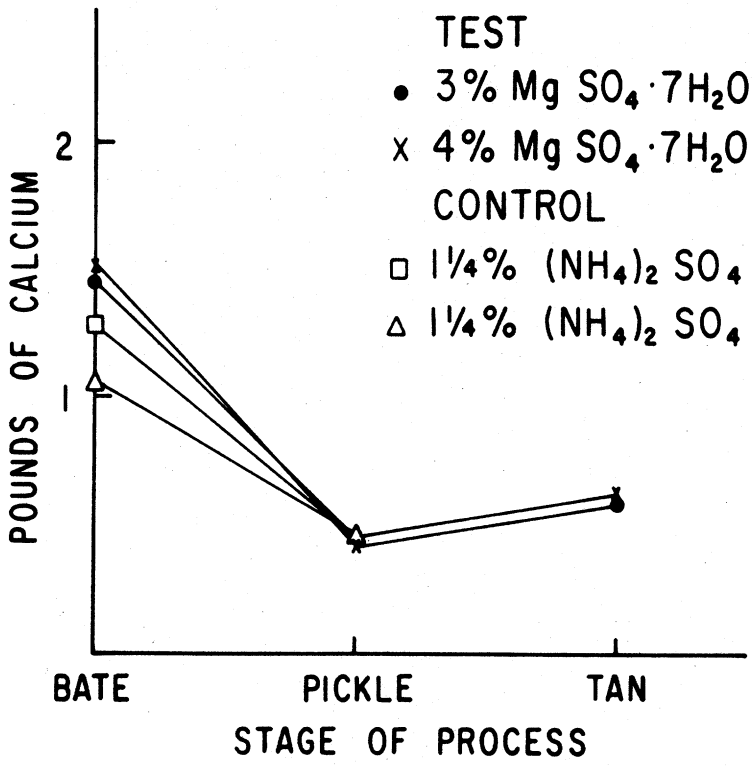

Figure 5. Pounds of calcium/1000 lbs of hides found in effluent after each processing stage.

in the pickle and tan stages and from the amount of chrome found in the tanned hide. The results are shown in Table VI. The calcium and chrome balances were run to test the sampling, for experience has shown that the best one could do was about 96% recovery for calcium and up to a 105% recovery for chrome. In experiment C, the magnesium balance was lower than one would like, however the calcium and the chrome recovery was satisfactory. Experiment D gave better results.

TABLE VI

MATERIAL BALANCE
OVERALL PERCENT RECOVERY

	Percent Recovery	
Parameter	Experiment C	Experiment D
Calcium	95.4	95.8
Magnesium	91.5	97.5
Chrome	98.0	98.0

Samples from experiments C and D were submitted for physical testing, and the results are shown in Table VII. The test is again compared to the standard process, and the results are comparable.

In the final experiment (E), a matched side study using the standard process as the control and 4% magnesium sulfate and 0.2% sulfuric acid was again run. The effluents from this experiment were collected and ammonia determination was performed. Figure

TABLE VII

EFFECT OF DELIME-BATE PROCESS VARIATIONS ON PHYSICAL PROPERTIES OF CRUST

Parameter	$MgSO_4 \cdot 7H_2O$		$(NH_4)_2SO_4$	
	Mean[a]	SD	Mean[b]	SD
Tensile (psi)	2566.2	978.9	2264.6	457.4
Extension (%)	51.2	5.8	43.5	7.3
Ball Burst (lbs)	156.0	19.1	125.9	21.6
Stitch Tear (lbs)	64.6	14.2	73.0	13.7
Thickness (inches)	0.0705	0.0028	0.0708	0.0027

[a] N = 8.
[b] N = 12.

6 rather dramatically shows how the effluent load is affected by the use of ammonia in deliming. Protein breakdown contributes a small amount as indicated by the curve.

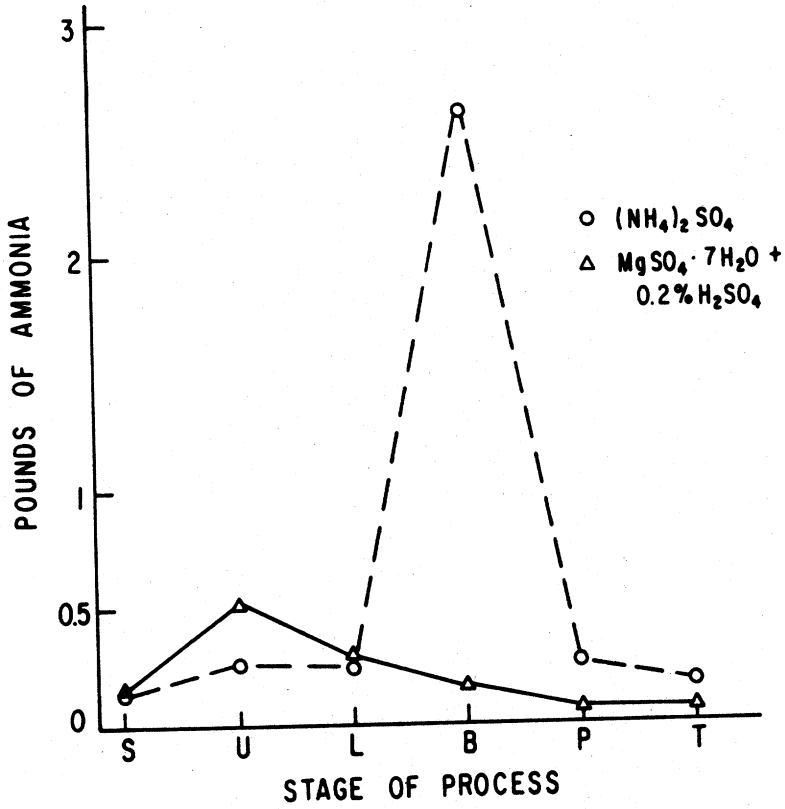

Figure 6. Pounds of ammonia/1000 lbs of hides found in effluent after deliming with magnesium sulfate and ammonium sulfate.

The blue stock from this experiment was sent to cooperating tanneries for finishing and for evaluation. Overall assessment of the leather was that it had a good break and a flat grain. However, it did not have the clarity that one would need for an aniline type finish. Possibly the bate was not activated, for it was after this stage that the leather did not look as clean as that resulting from the standard process. This is an area in which further research could be warranted.

Conclusion

It was found from bench scale and pilot scale experiments that magnesium sulfate and sulfuric acid was effective in the deliming of hides. However the Koopman process had to be modified to keep the pH under control. The process could be applicable to cattlehide processing if one makes changes in the formula, as Constantin (6-7) contended.

Acknowledgements

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